



Rational design of defect metal oxide/covalent organic frameworks Z-scheme heterojunction for photoreduction CO₂ to CO

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ABSTRACT

Z-scheme heterostructure consisting of covalent organic frameworks (COF) and inorganic semiconductor possesses tremendous potential for achieving efficient photoreduction of CO₂. However, the precise design and rationalization of the interaction between COF and inorganic semiconductors remains a great challenge. Herein, the interaction of different N-sites on T-COF framework with defect TiO₂ and stoichiometric TiO₂ is investigated by density functional theory. The theoretical analysis suggests that the amine group of T-COF could provide an energetically favored binding site towards defect TiO₂. Accordingly, a stable Z-scheme heterostructure with well-defined chemical bonding between Ti³⁺ and -NH₂, and well-engineered geometry configuration through *in situ* anchoring defect TiO₂ on the surface of amine-functionalized T-COF sphere is designed. The obtained heterostructure exhibits a high CO₂-to-CO conversion efficiency, with nearly 100 % CO selectivity and an apparent quantum efficiency of 6.81 % at 365 nm. This work could provide guidance for the rational design of Z-scheme heterostructure photocatalysts for photocatalytic applications in high efficiency.

1. Introduction

The energy conversion strategies, such as carbon dioxide conversion, water splitting and nitrogen reduction, offer promising routes for building a sustainable and environment friendly energy cycle [1–3]. In these strategies, covalent organic frameworks (COF), including porphyrin-based COF, bipyridine-based COF and triazine-based COF are commonly utilized as a state-of-the art photocatalyst for the CO₂ reduction, hydrogen evolution reaction and nitrogen reduction [4–10]. However, it is difficult for a single COFs to serve as photocatalyst to simultaneously satisfy all the requirements for industrial photocatalytic efficiency, such as strong redox ability, high charge separation efficiency, wide light absorption range and long-term stability. Instead of developing novel framework construction, coupling with other semiconductor to form heterojunction is an alternative strategy to enhance

the performance of COF catalysts [11–13]. For instance, heterojunction composites fabricated from COF and other inorganic semiconductors, such as α-Fe₂O₃, Bi₂WO₆, TiO₂, etc., have been intensively investigated, and they exhibited an enhanced performance over those only have a single phase structure [14–17]. Nevertheless, these kinds of COF-based photocatalysts still fail to meet the strict criteria including high selectivity and stability, mainly due to mismatched band structure for the specific product, undefined transmission channel for the charge delivery and weak interaction between them.

Recently, the electronic structure modulation is generally utilized to optimize energy band structure in the photocatalyst and achieve the better conversion efficiency, which have emerged as a research frontier in photocatalysis [18–20]. The defect engineering has been widely considered as promising approaches to modulate the electronic structure of metal oxide [21–23]. Compared to the stoichiometric metal oxide, the

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defective metal oxides exhibit improved the photogenerated charge-carriers transfer and separation efficiency [24,25]. In addition, it is important to build the well-defined electron transmission channel between the two components to achieve a rational design of optimal heterojunction photocatalysts [26–28]. Most recently, several interfaces connection models, such as van der Waals forces, electrostatic interaction, hydrogen bonding and chemical bonding, have been reported to correlate the existence of chemical bonding with the performance of photocatalyst, such as the tight and stable interface [29,30]. Therefore, it is imperative to design a Z-scheme system with the following characteristics. (i) well-defined structure with both components being exposed to reactive substrates and light irradiation; (ii) suitable defect introduction for the proper band structure; and (iii) specific chemical bond connection between the two composites for the fast migration and separation of electrons and holes. The coordinatively unsaturated metal centers for the metal oxide on the COF surface are good choice to address the above issues, which provides the defined structures for further investigation on the reaction mechanism. However, no practical strategies for effectively coupled the COF and deficient metal oxide semiconductor with specific metal–N covalent connection has been reported yet.

Herein, we present a theoretical-guided strategy of COF/defect-TiO₂ heterojunction photocatalyst for the selective reduction of CO₂ to CO. The adsorption energy using density functional theory (DFT) calculation suggests that the intrinsic deficient TiO₂ can be formed on the surface of NH₂–T–COF through Ti–N covalent bonding, where Ti³⁺–N on amino group is suggested to be the most active sites. Then, a stable Z-scheme system with well-engineered geometry configuration and intimately contacted heterointerface through anchoring defect TiO₂ on the surface of amine-functionalized COF sphere, is prepared. The Ti–N bonding between D-TiO₂ and NH₂–T–COF not only results in a well-combined interface, but acts as a good electrons delivery channel between them, forming a direct Z-scheme heterostructure. The obtained NCTS-2 heterostructure exhibits an excellent activity for photocatalytic CO₂ reduction, giving a 7.51 μmol of CO in a 4 h reaction with a nearly 100 % CO selectivity and an apparent quantum efficiency of 6.81 % at 365 nm, much higher than that of pure D-TiO₂. *In situ* DRIFTS results suggest that the significantly enhanced catalytic activity and selectivity are ascribed to the synergistic effect of Ti sites and rich-N groups of NH₂–T–COF framework, in which the rich-N groups not only serve as a host for CO₂ molecules and Ti sites, but also facilitate the activation of CO₂ molecules and inhibit the competitive H₂ evolution. This work highlights that building the Z-scheme COF system with specific bonding between the components not only provide a tight and stable interface as well as a definite electrons delivery channel, but also regulate active sites, which jointly improve CO₂RR performance in the CO production.

2. Experimental section

2.1. Materials

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine and 1,3,5-benzene tricarboxaldehyde were purchased from Yanshen Technology (Jilin, Changchun, China). Tetrabutyl titanate (TBT) was brought from Sino-pharm (Shanghai, China). CO₂ (99.99 %) were purchased from Saizhong Gas (Changsha, China). All other solvents and reagents were obtained from commercial sources and used without further purification unless otherwise noted.

2.2. Synthesis of NH₂–T–COF

NH₂–T–COF was prepared according to the procedures of T–COF. [16] Here, excessive 4,6-tris(4-aminophenyl)-1,3,5-triazine (0.05 mmol, 17.2 mg) and 1,3,5-benzenetricarboxaldehyde (0.04 mmol, 6.5 mg) were used as monomers to construct NH₂–T–COF. The reaction conditions were the same as for T–COF.

2.3. Synthesis of D-TiO₂

The D-TiO₂ was synthesized by modified literature procedures [31]. 0.5 mL of TBT was added to 15 mL of ethanol followed by vigorous stirring for 30 min. Then, 50 μL of hydrofluoric acid (40 %) and 1.5 mL of deionized water were added dropwise to the reaction system, respectively. Then stirring for another 30 min, the resulting solution was transferred into Teflon-lined autoclave (50 mL) and subsequently kept at 120 °C for 24 h. After the reaction was cooled to room temperature, the precipitate was collected, washed with ethanol, then dried under vacuum at 60 °C for 8 h.

2.4. Synthesis of NCTS

NH₂–T–COF (40 mg) was fully dispersed in the ethanol solvent (15 mL). Then, a certain amount of TBT was added to the solution following vigorous stirring for 30 min. After that, 10 μL of hydrofluoric acid (40 %) and 300 μL of deionized water were added dropwise to the reaction system, respectively. Then stirring for another 30 min, the resulting solution was transferred into Teflon-lined autoclave (50 mL) and subsequently kept at 120 °C for 24 h. After the reaction was cooled to room temperature, the precipitate was collected, washed with ethanol, then dried under vacuum at 60 °C for 8 h. By varying the amount of the precursor TBT (40, 65, 90 μL), NCTS-X with different D-TiO₂ content were obtained (X = 1, 2, 3).

2.5. Photocatalytic CO₂ reduction reaction

The photocatalytic CO₂ reduction reaction was performed in a closed gas circulation system (Labsolar 6A, Beijing PerfectLight) under full solar-spectrum irradiation. Typically, the as-prepared photocatalyst (10 mg) was dispersed in a mixed solution of 50 mL acetonitrile and 30 mL ascorbic acid aqueous (0.1 M). Then, the obtained suspension solution was transferred to a Quartz and Pyrex glass hybrid reaction cell. After completing the evacuation of the air, ~80 kPa of pure CO₂ gas was injected into the airtight system. After adsorption equilibrium (~30 min), a 300 W Xe lamp (PLS-SXE300, PerfectLight, Beijing, China) was used at the top of the reactor as the light source, and cooling water was employed to control the temperature of the reaction system at 5 °C. The produced CO and H₂ was analyzed by gas chromatography (7890B, Agilent, CA, USA).

3. Results and discussion

3.1. Theoretical analysis

The interaction of different N-sites on T–COF framework [16] with defect TiO₂ and stoichiometric TiO₂ by density functional theory (DFT) calculations was investigated. As shown in Fig. S1, the rich-N groups on the T–COF skeleton are divided into three basic kinds: triazine (σ–N_{sp2}), imine (σ–N_{sp2}) and amine (σ–N_{sp3}) groups. As presented in Fig. 1a–1c, the adsorption energy (*E*_{ads}) between defect TiO₂ and N-sites of triazine, amine and imine groups are –0.68, –1.32, –1.90 eV, respectively, suggesting that amine groups possess more stronger interaction for defect TiO₂. This proves that D-TiO₂ binding is more energetically favored to amine groups than to triazine and imine groups during the process of D-TiO₂ growing on the T–COF framework. More significantly, the DFT calculations suggest that the *E*_{ads} of amine groups on T–COF framework toward defect TiO₂ (–1.90 eV) is much larger than that of defect-free TiO₂ (–0.52 eV), indicating that defect TiO₂ is more energetically favored to rivet on the T–COF framework (Fig. 1d). These findings manifest that amine group could provide a more favored energetically binding site towards defect TiO₂ formation on the surface of T–COF than the imine and triazine group, resulting in a more efficient defect TiO₂ loading, as well as a much tighter and more stable interface. Therefore, the incorporation of more amine group within T–COF

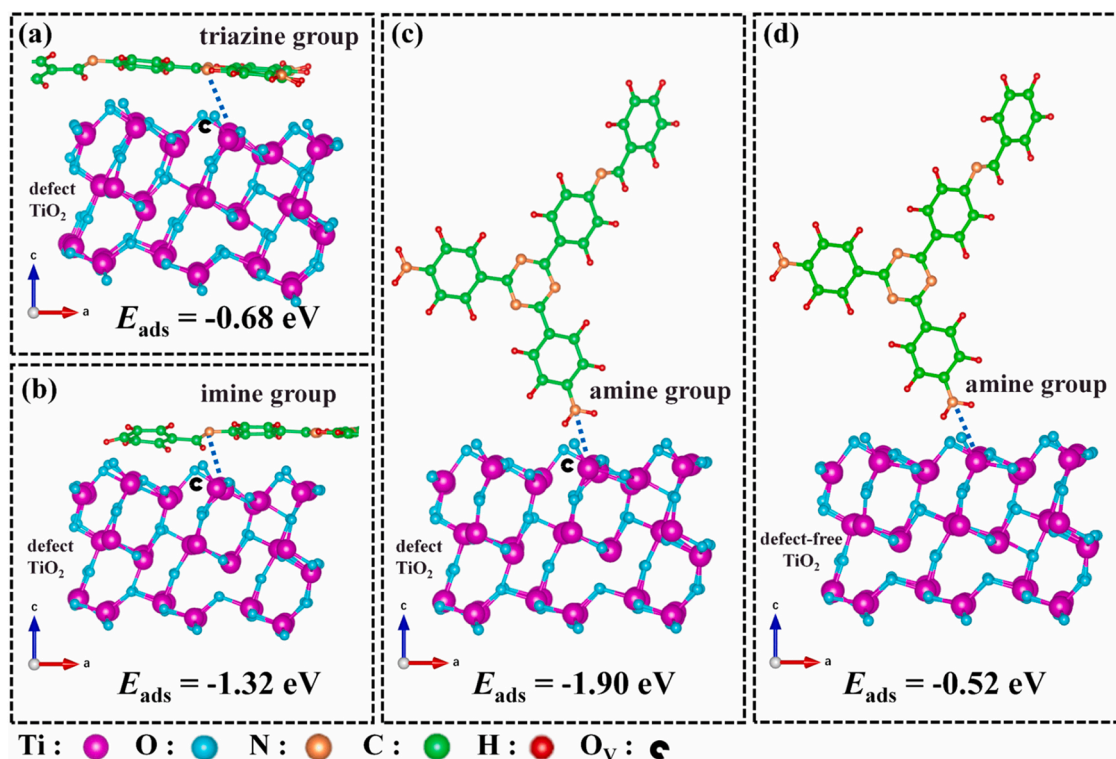


Fig. 1. Optimized structure model of different N-sites on T-COF framework adsorbed on the surface of defect TiO₂ and defect-free TiO₂. E_{ads} is the adsorption energy.

skeleton is an effective strategy to stabilize bonded defect TiO₂ for ultimate catalytic applications.

3.2. Synthesis and characterization of photocatalyst

Accordingly, we designed and fabricated surface-loaded defect TiO₂ (D-TiO₂) amine-functionalized T-COF (NH₂-T-COF). The preparation processes of NH₂-T-COF/D-TiO₂ spheres (NCTS) are illustrated in Fig. 2a. To ensure that the surface of the COF spheres loading more amine groups for TiO₂ binding, [32] amine-functionalized T-COF was synthesized by the condensation of 1,3,5-benzenetricarboxaldehyde and an excess of (2,4,6-tris(4-aminophenyl)-1,3,5-triazine (see the details in Supporting information). As shown in Fig. S2, the zeta potential of NH₂-T-COF is significantly lower than that of T-COF, indicating an increase in the number of amine groups on the surface of NH₂-T-COF. The elemental analysis also shows that the N and H elements on the skeleton of NH₂-T-COF are higher than those of T-COF (Table S1). These results demonstrate that the amine groups are successfully decorated on the surface of T-COF sphere. In the Fourier transform infrared (FT-IR) spectra of NH₂-T-COF (Fig. S3), the peak at 1686 cm⁻¹ attributed to the C=O stretching disappears, manifesting a high degree of polymerization. The crystallinity of NH₂-T-COF was confirmed by powder X-ray diffraction (PXRD). All peaks match well with those of the simulated AA stacking mode. And the peak at 5.65° shows a high intensity, indicating the successful preparation of NH₂-T-COF with high crystallinity (Fig. S4) [33]. Then, different masses of tetrabutyl titanate (TBT) as the precursor are uniformly dispersed on the surface of NH₂-T-COF sphere, following by one-step solvothermal reaction to obtain the defect TiO₂-decorated NH₂-T-COF spheres composites (NCTS). Thermogravimetric analysis (TGA) shows their excellent thermostability without obvious mass loss after heating up to 200 °C under N₂ atmosphere (Fig. S5).

The morphology of the samples was recorded by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As illustrated in Fig. 2b and S6, after *in situ* modification of D-TiO₂ on

NH₂-T-COF, the as-obtained NCTS still maintains the spherical morphology of NH₂-T-COF, and D-TiO₂ nanoparticles can be clearly seen uniformly embedded on the surface of NH₂-T-COF spheres (Fig. 2c). The high-resolution TEM (HRTEM) image clearly shows the lattice fringes with an interplanar spacing of 0.352 nm, which is attributed to the (101) plane of anatase TiO₂ (Fig. 2d) [34]. Moreover, the high-angle annular dark field TEM (HAADF-TEM) image and energy-dispersive X-ray spectroscopy (EDX) elemental mapping of NCTS-2 further prove that Ti element are evenly distributed within the framework of NH₂-T-COF sphere (Fig. 2e-h). It should be noted that the pure D-TiO₂ prepared by the same solvothermal method exhibits an agglomerated state (Fig. S7). After introduction of NH₂-T-COF, the D-TiO₂ nanoparticles can be uniformly dispersed on the surface of NH₂-T-COF sphere. These results manifest that the NH₂-T-COF framework can serve as the template to well anchor and stabilize D-TiO₂ by the strong interaction.

The PXRD pattern of NCTS composites are shown in Fig. 3a. The diffraction peaks at 5.65, 9.75, 11.25 and 14.95° correspond to the (100), (110), (200) and (210) facets of NH₂-T-COF respectively, in agreement with the XRD pattern of simulated AA stacking mode, [33] and the peaks at 25.28, 37.82, 48.05, 53.89 and 55.06° attribute to the (101), (004), (200), (105) and (211) facets of D-TiO₂, respectively (Fig. S8), matching up with the simulated PXRD patterns of the typical anatase TiO₂ (JCPDS No. 21-1272), which reveals that the crystal structure of the NH₂-T-COF and D-TiO₂ are basically unchanged after the formation of the heterostructure composite. The FT-IR spectra of NCTS-2, NH₂-T-COF and D-TiO₂ are shown in Fig. 3b. For pure D-TiO₂, the main peaks appearing at 400–700 cm⁻¹ are attributed to Ti–O stretching and another two broad peaks at about 3300–3500 and 1600–1650 cm⁻¹ correspond to the surface-adsorbed water and hydroxyl groups, respectively. These characteristic peaks all appear in the FT-IR spectra of NCTS-2, further suggesting the successful preparation of NCTS-2 heterostructure composite. As shown in Fig. S9, the newly formed C=N after polycondensation can be clearly observed in the solid-state ¹³C cross polarization magic angle spinning (¹³C CP-MAS)

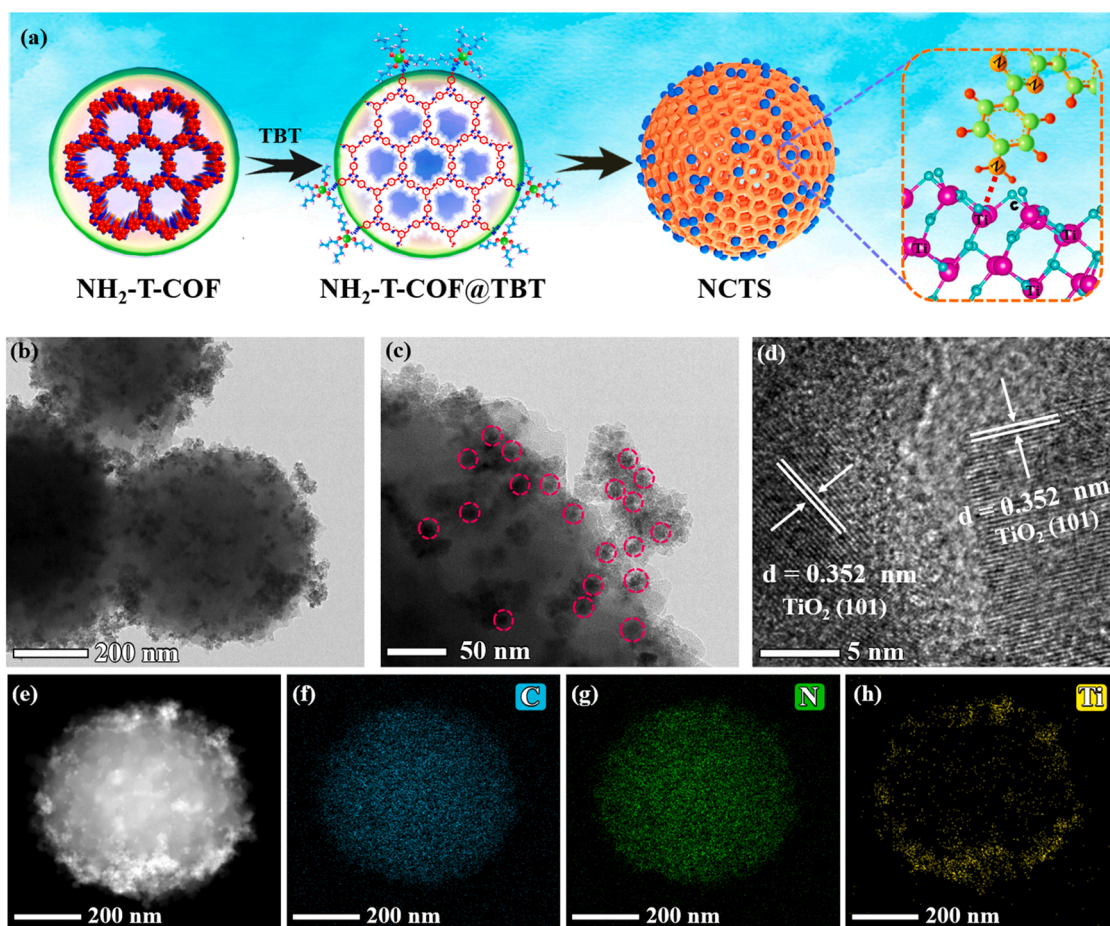


Fig. 2. (a) Schematic illustration of the preparation of NCTS. (b, c) TEM images of NCTS-2. (d) HRTEM image and lattice fringes of NCTS-2. (e) The HAADF-TEM image of NCTS-2. (f–h) EDX elemental mapping of NCTS-2.

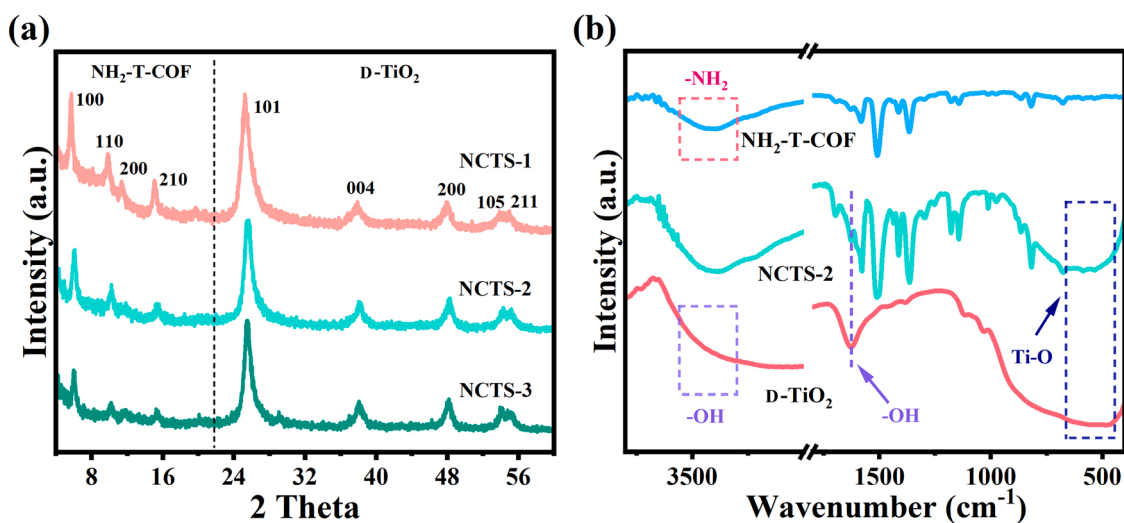


Fig. 3. (a) PXRD patterns of NCTS. (b) FT-IR spectra of NCTS-2, $\text{NH}_2\text{-T-COF}$ and D-TiO_2 .

NMR spectra of NCTS-2, which further proves that $\text{NH}_2\text{-T-COF}$ was not hydrolyzed and the structure is stable after loading defect TiO_2 .

The porosity features of these samples were evaluated by N_2 adsorption and desorption isotherms at 77 K (Fig. 4a). Brunauer–Emmett–Teller (BET) surface area of NCTS-2 was calculated to be $488.7 \text{ m}^2 \text{ g}^{-1}$, smaller than that of pure $\text{NH}_2\text{-T-COF}$ ($697.8 \text{ m}^2 \text{ g}^{-1}$) due to the presence of D-TiO_2 with a low surface area ($256.3 \text{ m}^2 \text{ g}^{-1}$). The

pore size of pure $\text{NH}_2\text{-T-COF}$ distributes at around 1.13 nm (Fig. 4b), which was further fitted by nonlocal density functional theory (NLDFT). And the average pore size distributions of NCTS-2 are centered at 3.12 nm because of the introduction of D-TiO_2 with mesoporous (3.61 nm). The plentiful porous structure offers great opportunity for the CO_2 molecules entering the pores and the exposed inner surface where the redox reactions occur. Furthermore, the D-TiO_2 mass content

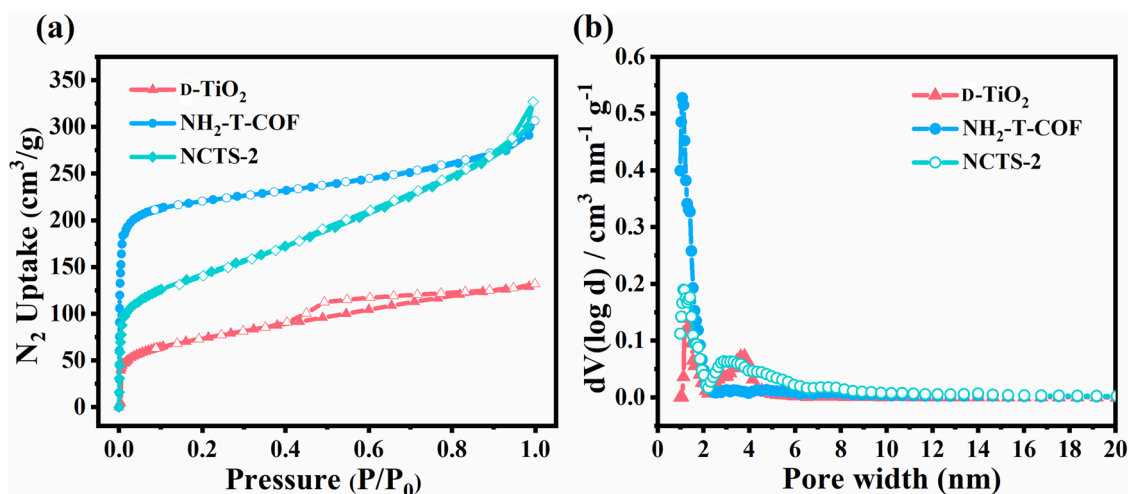


Fig. 4. (a) N₂ adsorption (solid symbols) and desorption (open symbols) isotherms of D-TiO₂, NH₂-T-COF and NCTS-2 at 77 K. (b) Pore size distribution profiles of D-TiO₂, NH₂-T-COF and NCTS-2.

of NCTS composite was investigated from inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement and listed as Table S2. The content of D-TiO₂ in the NCTS-1, NCTS-2 and NCTS-3 composites was calculated to be 16 %, 23 % and 32.2 %, respectively, consistent with the theoretical results. These results indicate that the D-TiO₂ semiconductors are tightly inlaid over the framework of NH₂-T-COF, confirming the feasibility of this strategy.

3.3. Electronic structure and interaction of NH₂-T-COF/D-TiO₂ heterostructure

The chemical compositions and states of the samples were tested by X-ray photoelectron spectroscopy (XPS). For N 1s spectra of NH₂-T-COF (Fig. S10), the peak at ~398.2 eV could be ascribed to sp² hybridized N (C–N=C), while the peak at ~401.6 eV belongs to the amino groups (C–N–H) on the surface of NH₂-T-COF sphere. Compare to NH₂-T-COF, the N 1s spectra of NCTS-2 composite shows an extra peak at ~397.1 eV (Fig. S11), which is assigned to the formed Ti–N bonding between NH₂-T-COF and D-TiO₂. For Ti 2p, as shown in Fig. 5a and S12, two peaks at about ~458.7 and ~464.3 eV are attributed to the Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}, respectively, while another two peaks at ~457.7 and ~463.2 eV are separately assigned to the Ti³⁺ 2p_{3/2} and Ti³⁺ 2p_{1/2}, respectively, suggesting the presence of Ti³⁺ defects in TiO₂ crystal structure. The intrinsic defects were further supported by

electron paramagnetic resonance (EPR) spectra. As shown in Fig. 5b, the intensive EPR signal located at g = 1.998 are all observed for D-TiO₂ and NCTS-2, further confirming the successful formation of Ti³⁺ defects.

To elucidate the electronic structure and coordination information, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the titanium (Ti) K-edge were performed. Normalized Ti K-edge XANES of Ti-foil, anatase phase TiO₂ (anat-TiO₂) and NCTS-2 were resolved in Fig. 6a. The relative intensities of peaks as well as the line shape of NCTS-2 is consistent with that of the reference anat-TiO₂, further indicating that the TiO₂ in the heterostructure composite is anatase type [35]. The three peaks at 4965–4980 eV (labeled A, B, and C in the inset of Fig. 6a) are clearly observed, which can be assigned to the characteristic pre-peaks in the anatase Ti k pre-edge region by most of the experimental and theoretical works [36]. Obviously, the intensity of the pre-peak B of NCTS-2 is relatively lower than that of anat-TiO₂, suggesting that the average oxidation state of the Ti⁴⁺ species of NCTS-2 decreased. The results display that Ti⁴⁺ is partially reduced and formed Ti³⁺ defects during solvothermal processes [35–37], which is consistent with the XPS and EPR results. Then, Fourier transform (FT) of EXAFS spectrum in R-space at the Ti K-edge is further presented to provide coordination information (Fig. 6b). Compared with anat-TiO₂, the first peak of NCTS-2 shifts negatively, which is thought to correspond to the formation of Ti–N bonds.

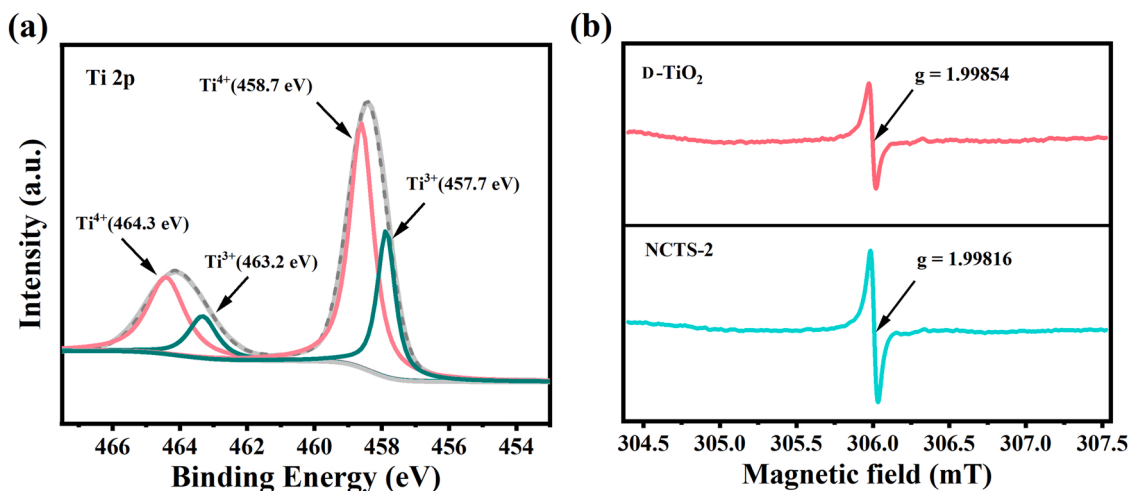


Fig. 5. (a) The Ti 2p XPS spectrum of NCTS-2. (b) EPR spectra of D-TiO₂ and NCTS-2.

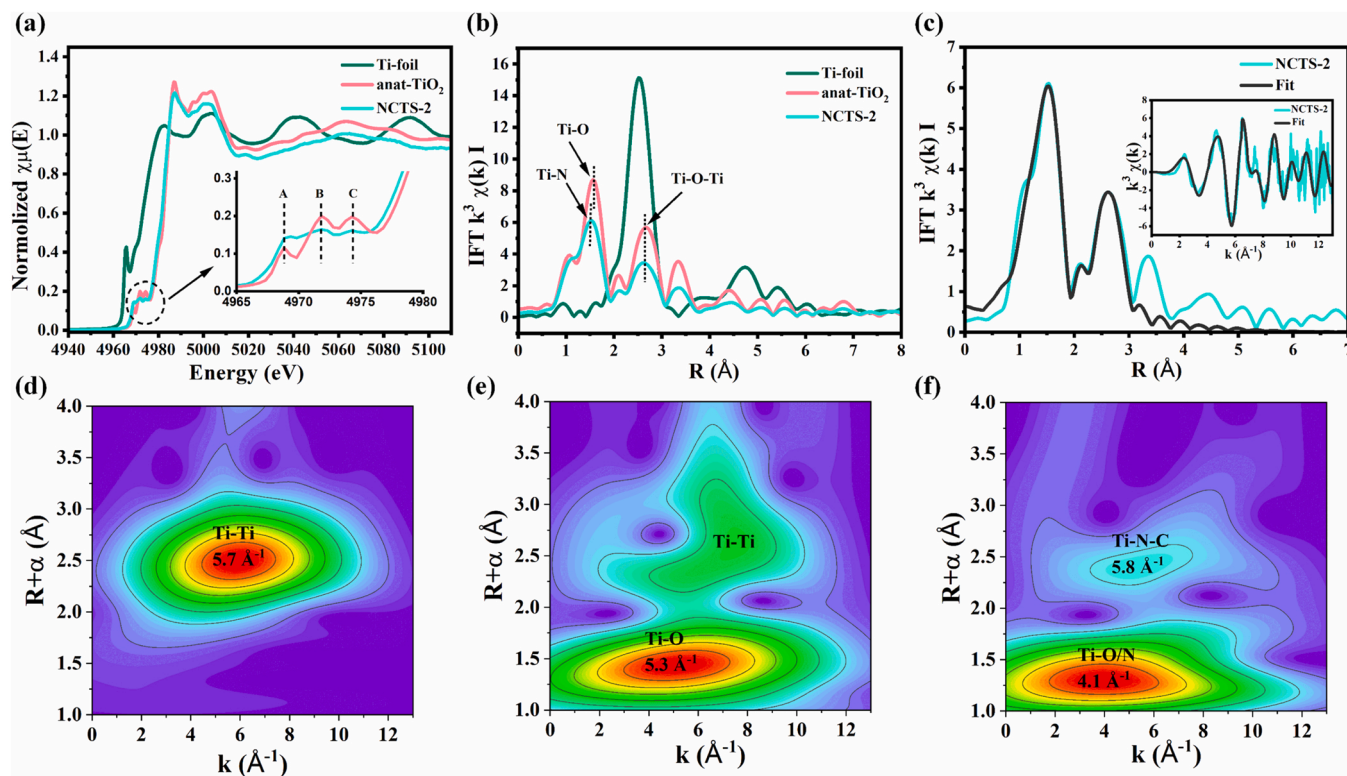


Fig. 6. (a) XANES spectra at the Ti K-edge of NCTS-2 sample, anat-TiO₂ and Ti-foil. (b) Fourier transform (FT) at the Ti K-edge of NCTS-2 sample, anat-TiO₂ and Ti-foil. (c) Corresponding EXAFS fitting curves of NCTS-2 at R space and (inset) k space. (d-f) Wavelet transform (WT) of Ti-foil, anat-TiO₂ and NCTS-2 sample.

To confirm the coordination information of Ti throughout the heterostructure NCTS-2, wavelet transform (WT) of Ti K-edge EXAFS oscillations was performed. From the WT contour plots of Ti-foil and anat-TiO₂ (Figs. 6d and 6e), it can be observed that the intensity maxima at 5.7 Å⁻¹ and 5.3 Å⁻¹ is associated with the Ti-Ti and Ti-O contribution, respectively. The WT contour plot of NCTS-2 (Fig. 6f) displays one maximum intensity at 4.1 Å⁻¹ and one at 5.8 Å⁻¹, which can be ascribed to the Ti-O/N first coordination shell and Ti-N-C second coordination shell, respectively [36,38]. EXAFS fitting was performed to extract the structural parameters of Ti atoms (Fig. 6c). The obtained coordination number of the center atom Ti is about 6 (Table S3), owing to the contribution N and O atoms. These results indicate that d-TiO₂ was firmly riveted on the NH₂-T-COF framework by the coordination with N atoms, as a result of stable heterostructure with strong interfacial interactions between d-TiO₂ and NH₂-T-COF.

3.4. Band structure and Z-scheme charge-transfer behaviors

The light-harvesting capability and electronic band structure of the samples were investigated by UV-vis diffuse reflectance spectroscopy (DRS) and Mott-Schottky measurement. As shown in Fig. 7a and S13, d-TiO₂, NH₂-T-COF and NCTS-2 exhibit sharp absorption edges at about 400, 470, and 465 nm, respectively. Compared to d-TiO₂, the absorption edge of all NCTS samples undergoes an obvious red shift and extends to the visible light region, which was initiated by the incorporation of NH₂-T-COF. Based on Tauc plot (Fig. S14) [5], the band gap values (E_g) of d-TiO₂ and NH₂-T-COF are estimated to be about 3.10 and 2.65 eV, respectively. Mott-Schottky (MS) measurements were conducted to determine the flat band potential of the samples (Fig. S15) [39]. The flat band potential of d-TiO₂ and NH₂-T-COF are determined as -0.05 and -0.40 V (vs. RHE). Namely, the conduction band (CB) position of d-TiO₂ and NH₂-T-COF can be roughly estimated as -0.25 and -0.60 V (vs. RHE) [40]. Combined with the E_g value of d-TiO₂ and NH₂-T-COF from UV/Vis DRS plot, the valence band (VB) position of

them can be evaluated as 2.85 and 2.05 V (vs. RHE) and outlined in Fig. 7b.

The work function (WF) was performed to estimate the charge transfer direction at the interface of the heterostructure consisted of d-TiO₂ and NH₂-T-COF. As illustrated in Figs. 7c and 7d, the work function of d-TiO₂ and NH₂-T-COF are 5.10 and 4.85 eV, respectively (Fig. S16), that is, the Fermi level (FL) of d-TiO₂ is lower than that of NH₂-T-COF, which indicates that the electrons on NH₂-T-COF will flow to d-TiO₂ until their Fermi level reaches equilibrium state after the formation of heterostructure composite. Then the built-in electric field is formed with the direction from NH₂-T-COF to d-TiO₂ at the interface. Since the direction of the photo-generated electric field is opposite to that of the built-in electric field, when light illuminated, the photoexcited electrons located on the CB of d-TiO₂ will recombine with the holes on the VB of NH₂-T-COF, forming a Z-scheme charge transfer process at the heterojunction interface between NH₂-T-COF and d-TiO₂.

The charge transfer pathway is shown in Fig. 7g and further validated by spin-trapping electron spin resonance (ESR) spectra. We utilized 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to probe the formation of hydroxyl radical (\cdot OH) and superoxide radical (\cdot O₂). As Figs. 7e and 7f show, under the illumination of Xenon lamp for 5 min, the typical peaks of DMPO- \cdot OH spin adduct with 1:2:2:1 quadruple signal can be obviously observed in the spectra of d-TiO₂, while the peaks intensity of DMPO- \cdot O₂ spin adduct are very weak. The result indicates that d-TiO₂ favors the generation of hydroxyl radical (\cdot OH) rather than superoxide radical (\cdot O₂), which ascribes its more positive VB potential (2.85 V) than that of H₂O/ \cdot OH (1.9 V, pH = 7). [41] For pristine NH₂-T-COF photocatalytic system, the characteristic signal of DMPO- \cdot O₂ spin adduct can be clearly observed, whereas the signal of DMPO- \cdot OH is almost undetectable, manifesting that the pure NH₂-T-COF is favorable for producing \cdot O₂ rather than \cdot OH radical due to its more negative CB potential than that of O₂/ \cdot O₂ (0.33 V) [42,43]. For the heterostructure composite NCTS-2 consisted of d-TiO₂ and NH₂-T-COF, both signals of DMPO- \cdot OH and DMPO- \cdot O₂ adducts are significantly enhanced than

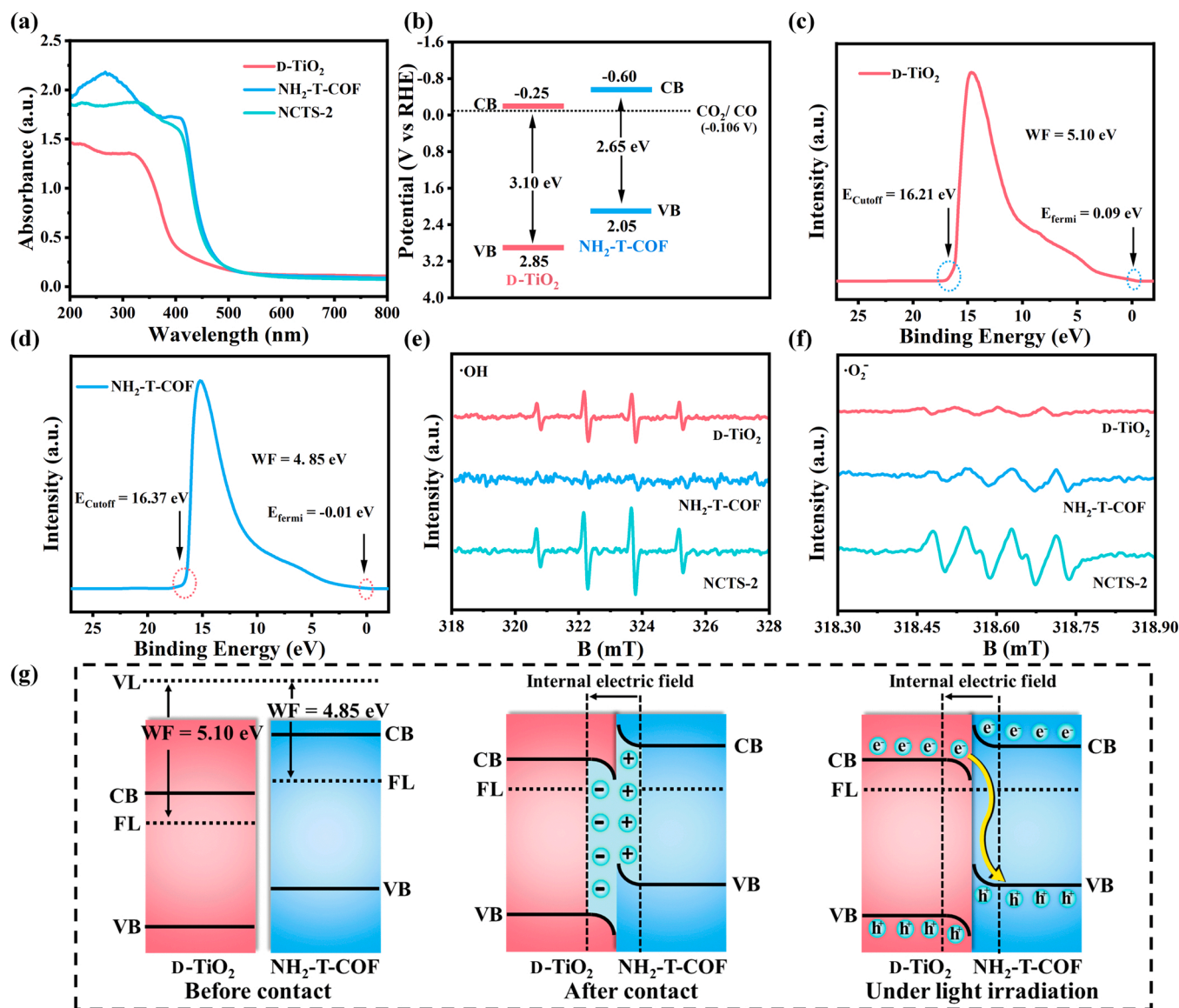


Fig. 7. (a) UV-visible DRS spectra of D-TiO₂, NH₂-T-COF and NCTS-2. (b) The estimated band structure of D-TiO₂ and NH₂-T-COF. UPS spectra of (c) D-TiO₂ and (d) NH₂-T-COF. DMPO spin-trapping ESR spectra recorded for (e) ·OH and (f) ·O₂⁻ under light irradiation for D-TiO₂, NH₂-T-COF and NCTS-2. (g) Schematic illustration of the relative band positions and charge transfer process of D-TiO₂ and NH₂-T-COF before contact, after contact and under light irradiation.

those of pure D-TiO₂ and NH₂-T-COF, which reveals that NCTS-2 owns both the strong oxidation ability of D-TiO₂ and the reduction property of NH₂-T-COF. These results indicate that the photogenerated electrons and holes of NCTS-2 are spatially separated on the semiconductors with higher reduction potential and oxidation potential, respectively, resulting in the Z-scheme migration path of photoelectrons. Moreover, high-resolution *in situ* X-ray photoelectron spectroscopy (XPS) spectra show that under light irradiation, the binding energy of Ti 2p shifts positively compared to that of in the dark, whereas the binding energy of N 1s shows a negatively shift (Fig. S17), which demonstrates that the excited electrons transfer from D-TiO₂ to NH₂-T-COF under illumination, further proving a Z-scheme charge-transfer path at the interface of NCTS-2 heterostructure. Therefore, under light irradiation, the electrons clustered at the CB of D-TiO₂ can recombine with the holes accumulated in the VB of NH₂-T-COF via a tight chemical bonding and stable interface, then the electrons and holes with higher reduction potential and oxidation potential can be well-preserved to participate in the redox reactions.

The interfacial Z-scheme charge-transfer behavior was further

measured by photoluminescence spectra (PL) and photoelectrochemical measurements. As the PL spectra shows in Fig. S18, the emission intensity observed from NCTS-2 is much weaker than that of D-TiO₂ and NH₂-T-COF, indicative of the low recombination rate of photoexcited electron-hole pairs after formation of the Z-scheme heterostructure. To explore the effect of interfacial interaction of the heterostructure on charge-transfer behavior, the NCTS-2 counterpart consisting of defect-free TiO₂ and NH₂-T-COF (defect-free NCTS-2) was synthesized (Fig. S19). As depicted in Fig. 8a, the transient photocurrent response of NCTS-2 exhibits a significantly enhancement of photocurrent intensity compared to pure D-TiO₂ and NH₂-T-COF, suggesting its greatly improved separation/transfer efficiency of the photogenerated electrons/holes after the constitution of heterojunction composite. Significantly, the photocurrent intensity of NCTS-2 is much higher than that of defect-free NCTS-2, which suggests that the strong interaction between D-TiO₂ and NH₂-T-COF not only provide a tight and stable interface, but also significantly promote the migration and separation of electrons and holes. Additionally, electrochemical impedance spectroscopy (EIS) displays that NCTS-2 shows the smallest radius of the high-frequency

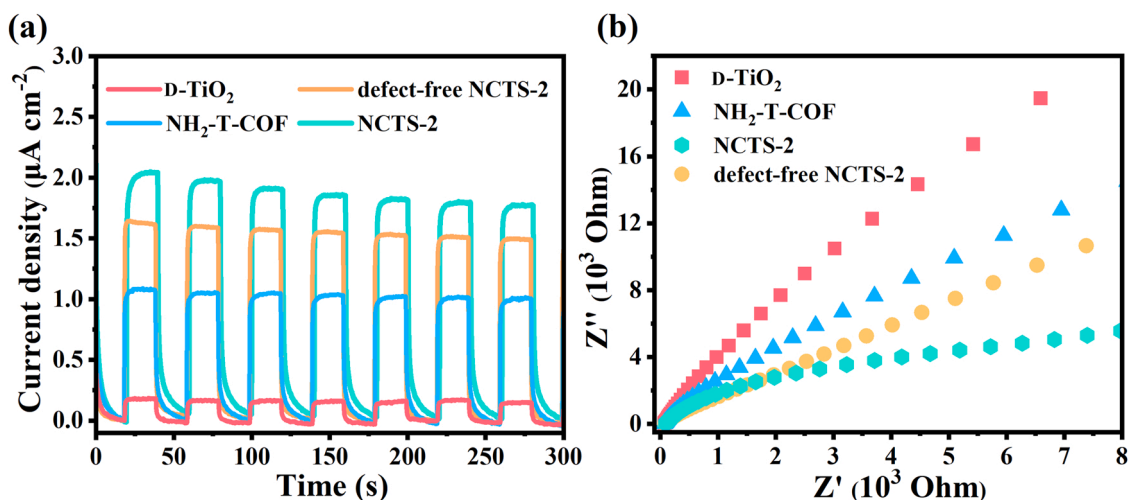


Fig. 8. (a) Transient photocurrent responses of D-TiO_2 , $\text{NH}_2\text{-T-COF}$, NCTS-2 and defect-free NCTS-2. (b) Electrochemical impedance spectroscopy of D-TiO_2 , $\text{NH}_2\text{-T-COF}$, NCTS-2 and defect-free NCTS-2.

semicircle with respect to all sample (Fig. 8b), indicating its higher conductivity than that of D-TiO_2 , $\text{NH}_2\text{-T-COF}$ and defect-free NCTS-2. These results demonstrate that the charges of NCTS-2 can be separated and transported in a Z-scheme route through the robust Ti–N bonding between D-TiO_2 and $\text{NH}_2\text{-T-COF}$, remaining the charges with higher redox capacity to participate the reaction. And compared to defect-free NCTS-2, the strong chemical bond connection between D-TiO_2 and $\text{NH}_2\text{-T-COF}$ can remarkably improve the charge separation efficiency, providing more opportunities for photogenerated charges to drive redox reaction.

3.5. Photocatalytic CO_2RR performance

The photocatalytic CO_2 reduction reaction (CO_2RR) performance of the photocatalysts was performed in a closed gas circulation system and evaluated under pure CO_2 (0.8 bar, 298 K) atmosphere in acetonitrile/water (5:3) mixture with ascorbic acid as sacrificial agent. Previous studies have confirmed that the CO_2 adsorption ability is beneficial to the improvement of the photocatalytic CO_2RR performance. The CO_2 adsorption isotherms were performed for the hybrid material NCTS-2, pure D-TiO_2 and $\text{NH}_2\text{-T-COF}$. As shown in Fig. 9a, NCTS-2 has a substantially improvement of CO_2 adsorption with an uptake of $58.1 \text{ cm}^{-3} \text{ g}^{-1}$ compared to pristine D-TiO_2 ($11.1 \text{ cm}^{-3} \text{ g}^{-1}$), attributing to the strong affinity between the rich-N groups in the framework of $\text{NH}_2\text{-T-COF}$ and CO_2 molecules. The increased CO_2 adsorption capacity of NCTS-2 complex is kinetically advantageous for CO_2 reduction. As expected, after 4 h of light irradiation, the NCTS-2 generated a maximum amount of CO of $7.51 \mu\text{mol}$, that is 9.3 times than that of pure D-TiO_2 ($0.81 \mu\text{mol}$) (Fig. 9b). Notably, D-TiO_2 produces a large amount of by-product H_2 during the progress of photocatalytic CO_2RR , while H_2 is hardly detected in the system of NCTS-2. In detail, the selectivity of pure D-TiO_2 to generate CO is only 15 %, but that of NCTS-2 composite is as high as nearly 100 %, which may give the credit to the substantial increase of CO_2 concentration at the reaction site. The kinetic curve of CO formation is shown in Fig. 9c and S20, all the NCTS hybrid samples display a significantly improved photocatalytic activity for CO evolution compared to pure D-TiO_2 and $\text{NH}_2\text{-T-COF}$. As the increase of D-TiO_2 on the surface of the $\text{NH}_2\text{-T-COF}$ sphere, the activity of NCTS-3 shows a decreasing trend. This may be due to the fact that excess D-TiO_2 will reduce the light-harvesting capability of $\text{NH}_2\text{-T-COF}$ as well as destroy its crystallinity. The poor crystallinity would be detrimental to the fast transfer of photoexcited electrons and holes, resulting in a decrease in the photocatalytic activity. By optimizing the loading of the precursor tetrabutyl titanate, the resultant NCTS-2 with 23% TiO_2 delivers the

highest photocatalytic CO_2RR performance. Notably, the CO formation rate of NCTS-2 is also faster than that of defect-free NCTS-2, indicating that the strong interfacial interactions and intimate contact interface between two semiconductors is very significant for the photocatalytic performance of heterostructure photocatalyst. To provide a reference for different comparison, the rates of CO evolution per gram of NCTS-2, D-TiO_2 and $\text{NH}_2\text{-T-COF}$ are listed as Fig. S21.

The apparent quantum yield (AQY) is a significant parameter to evaluate the performance of photocatalyst.[44] The AQY for photocatalytic CO evolution of NCTS-2, D-TiO_2 and $\text{NH}_2\text{-T-COF}$ were measured under the same reaction conditions but with different monochromatic light. The wavelength dependent AQY values are depicted as Fig. 9d, the AQY value of NCTS-2 was calculated to 1.41 % and 0.40 % at 365 nm and 420 nm, respectively. Moreover, the AQY value largely depends on the photocatalyst weight [45]. By optimization of the photocatalyst mass (Fig. 9e), the AQY value of NCTS-2 reaches 6.81 % at 365 nm, about 9 and 8 times better than that of pure D-TiO_2 (0.74%) and $\text{NH}_2\text{-T-COF}$ (0.83 %). Since the framework of COF and solvent also contain a large amount of carbon element, the isotope labeling experiment was performed to validate the carbon source of the resulting product originated from the photocatalytic CO_2RR process. We employed isotope-labeled carbon dioxide ($^{13}\text{CO}_2$) as an alternative source gas with NCTS-2 sample to complete the evaluation experiment. As shown in the mass spectra in Fig. 9f, ^{13}CO ($m/z = 29$) was finally detected, which proves that the generated CO originates from the reactant CO_2 rather than the decomposition of photocatalyst and solvent. Additionally, NCTS-2 photocatalyst ran for 24 h or 5 cycles, but its activity did not decrease significantly. (Fig. 9g and Fig. S22). The structural integrity and crystallinity of NCTS-2 retain after the long-term reaction, as proved by PXRD pattern and Roman spectra (Fig. 9h and i).

3.6. Mechanism of the activity enhancement

To further understand the mechanisms for photocatalytic CO_2RR on the catalysts, *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFTS) was conducted to investigate the processes of CO_2 adsorption and activation on NCTS-2 and D-TiO_2 . CO_2 can either act as a linear molecule, physically adsorbed on the catalyst surface, or as a bent molecule, chemisorbed on the catalyst surface. As shown in Figs. 10a and 10b, the DRIFTS of CO_2 adsorbed on both NCTS-2 and D-TiO_2 show two physisorption peaks at ~ 2363 and $\sim 2338 \text{ cm}^{-1}$ [46]. Note that the intensity of the peaks for NCTS-2 is obviously higher than D-TiO_2 , indicating that the adsorption capacity of NCTS-2 for CO_2 is significantly enhanced owing to the introduction of rich-N $\text{NH}_2\text{-T-COF}$. CO_2

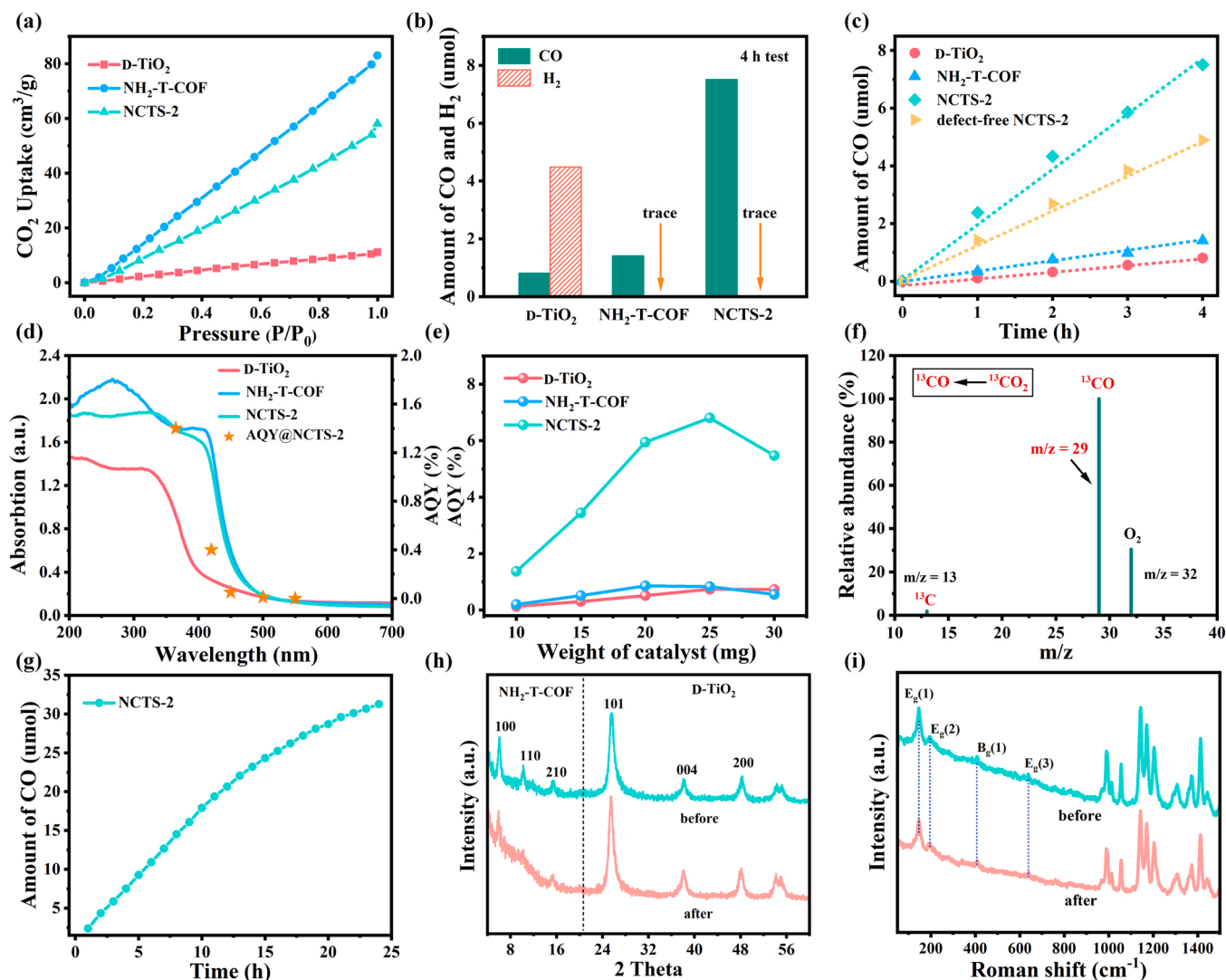


Fig. 9. (a) CO₂ adsorption curves of D-TiO₂, NH₂-T-COF and NCTS-2 measured at 273 K. (b) Photocatalytic CO₂RR performance of D-TiO₂, NH₂-T-COF and NCTS-2. (c) Time-dependent CO production performance using D-TiO₂, NH₂-T-COF, NCTS-2 and defect-free NCTS-2 as photocatalyst. (d) AQY values of NCTS-2 (10 mg) under different monochromatic light irradiation and UV/Vis DRS plot. (e) AQY values of D-TiO₂, NH₂-T-COF and NCTS-2 at different photocatalyst weights under 365 nm. (f) Mass spectra of ¹³C produced from the photocatalytic reduction of ¹³CO₂ over NCTS-2. (g) Photocatalytic durability test of NCTS-2. (h) PXRD pattern and (i) Raman spectra of NCTS-2 before and after photocatalytic CO₂RR.

chemisorption results in the formation of partially charged CO₂^{δ-} species through interactions with surface atoms of catalyst [47]. As depicted in Fig. 10c, the chemisorption peak at ~1517 cm⁻¹ corresponds to monodentate carbonate (m-CO₃²⁻), and those at 1328 and 1590 cm⁻¹ assign to bidentate carbonate (b-CO₃²⁻), while D-TiO₂ has only the signal of m-CO₃²⁻, but no signal of b-CO₃²⁻ (Fig. 10d) [13,46,48]. For D-TiO₂, the presence of m-CO₃²⁻ signal indicates that the Type I CO₂ adsorption mode (Fig. 10e) can be formed on the surface of D-TiO₂, due to the interaction between carbon atom of the CO₂ molecule and titanium/oxygen atoms on the surface of D-TiO₂. For NCTS-2 composite, the appearance of b-CO₃²⁻ signals manifests that Type II, Type III and Type IV CO₂ adsorption modes may coexist [47,49,50]. However, the oxygen coordination mode (Type II and Type III) has been proved that the final product is formic acid (HCOOH) rather than carbon monoxide (CO) because the breaking of the C-O bond in the CO₂ molecule does not occur in this situation [51]. As for the carbon (Type I) or mixed coordination mode (Type IV), the anchoring of the carbon atom on the surface of catalyst makes them difficult to undergo hydrogenation and is more favored to produce CO [51]. Therefore, the mixed coordination mode (Type IV) is the main adsorbed CO₂^{δ-} species on the surface of

NCTS-2, due to the synergistic adsorption and activation for CO₂ molecule through the nitrogen atoms of NH₂-T-COF framework and the titanium/oxygen atoms of D-TiO₂. Both NCTS-2 and D-TiO₂ show the bicarbonate (HCO₃⁻) signals due to the interaction of hydroxyl groups on the surface of sample with CO₂ molecules. All these carbonate and bicarbonate species are bent to lose the linear symmetry of free CO₂ molecules, then achieve further activation by accepting electrons. The peaks at about 1607 and 1248–1278 cm⁻¹ are attributed to CO₂⁻ intermediates, indicating that the adsorbed CO₂ molecules can be successfully activated on the surface of NCTS-2 and D-TiO₂, and then transform into product CO [48,52,53].

Compared to D-TiO₂, the introduction of amine-functionalized COF provides more adsorption and activation sites for CO₂, which is important for suppressing the competitive HER to increase the selectivity towards CO product of NCTS-2 photocatalyst (Fig. 10f). Moreover, the mixed carbon-oxygen coordination on the surface of NCTS-2 leads to more stable arrangements than the pure carbon coordination on the surface of D-TiO₂. Thus, the mixed coordination is more energetically favored to achieve further activation to form CO₂⁻ intermediate that is always considered as the rate-limiting step [49]. Although the formation

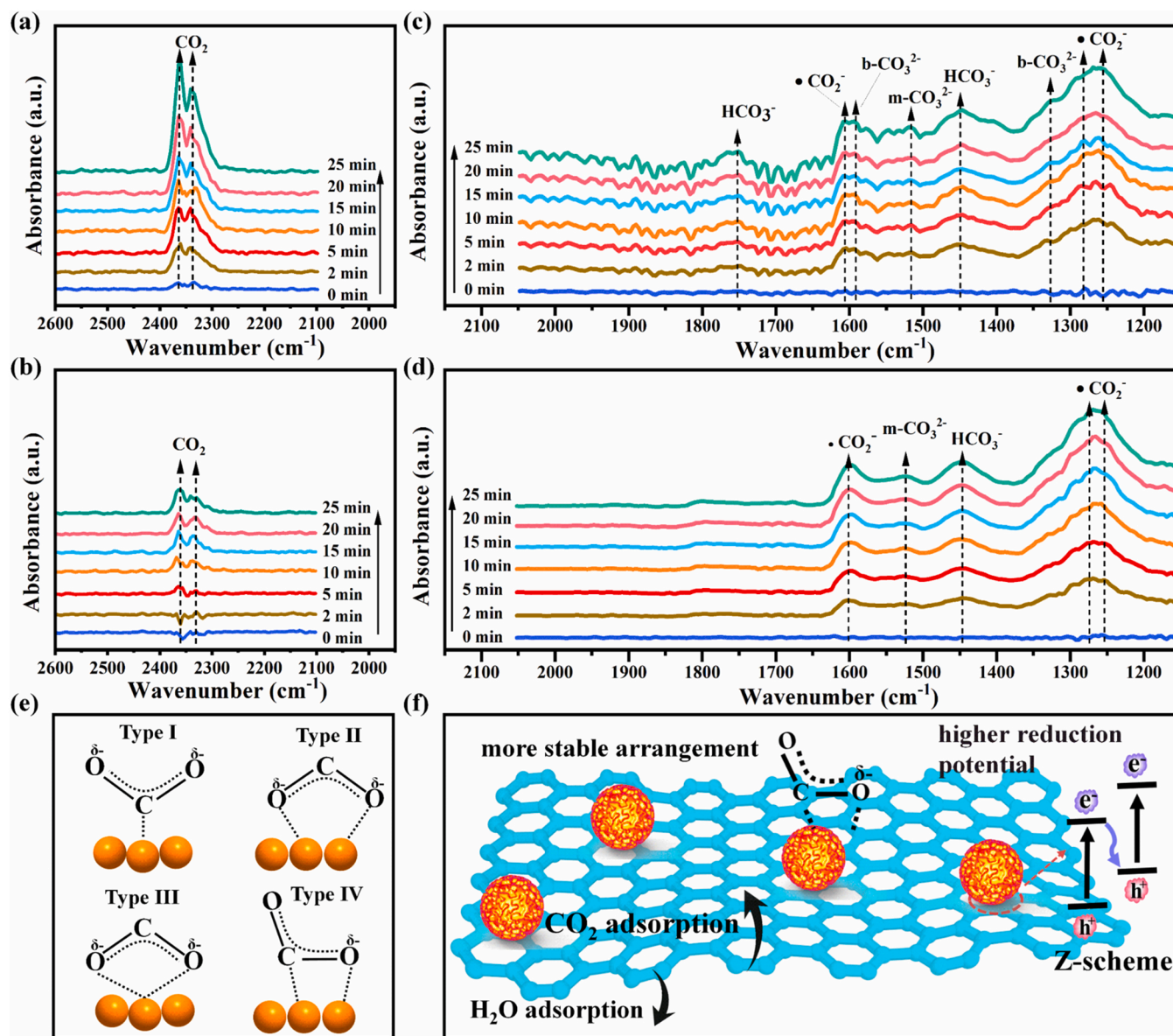


Fig. 10. *In situ* DRIFTS measurement of NCTS-2 (a, c) and d-TiO₂ (b, d) in the presence of H₂O and CO₂ under constant simulated solar illumination. (e) The possible adsorbed CO₂^{δ-} species on d-TiO₂ and NCTS-2. (f) Schematic diagram of important reasons for the excellent photocatalytic CO₂RR performance of NCTS-2 heterostructure.

of the bent CO₂^{δ-} species can reduce the overpotential to form $\cdot\text{CO}_2^-$ intermediate, the formation of both $\cdot\text{CO}_2^-$ intermediate and CO still requires sufficient driving force from photogenerated electrons to achieve. NCTS-2 as Z-scheme heterostructure, the photogenerated electrons with higher reduction potential are preserved, so NCTS-2 has more driving force to carry out the one-electron reduction of CO₂ to $\cdot\text{CO}_2^-$ (or $\cdot\text{CO}_2^-$ to CO) than pure d-TiO₂. Based on the above discussion, a possible mechanism of the CO₂ reduction over NCTS-2 is proposed. The $\cdot\text{CO}_2^-$ intermediate obtained by CO₂ adsorption and activation is bound to N/Ti atoms of NCTS-2 through the carbon atom. The oxygen atom in $\cdot\text{CO}_2^-$ would combine with a hydrogen atom to form the carboxyl radical. The process of bonding hydrogen would lead to breaking the bond between this oxygen atom and the carbon atom and then disintegrates into the carbon monoxide.

4. Conclusions

In summary, we present a theory-guided design of a stable COF-

based Z-scheme heterostructure with well-engineered geometry configuration and intimate contact interface by *in situ* anchoring defect TiO₂ on the surface of amine-functionalized T-COF sphere for photocatalytic CO₂ reduction. EPR spectra combining XPS results and Ti K-edge EXAFS prove the successful formation of Ti³⁺ defects and the presence of N-Ti chemical bonding. The Ti-N bonding between d-TiO₂ and NH₂-T-COF not only results in a well-combined interface, but also acts as a good electrons delivery channel between them, forming a Z-scheme heterostructure with a low charge transfer resistance. The designed NCTS-2 heterostructure photocatalyst displays an excellent activity and selectivity for photocatalytic CO₂ reduction to CO. Compared to pure d-TiO₂, the significantly enhanced photocatalytic activity and selectivity of NCTS-2 attribute to following aspects: i) the introduction of amine-functionalized COF provides more adsorption and activation sites for CO₂; ii) the synergistic effect of Ti sites and rich-N groups of NH₂-T-COF framework energetically favors to form $\cdot\text{CO}_2^-$ intermediate that is always considered as the rate-limiting step; and iii) NCTS-2 as Z-scheme heterostructure possesses higher reduction

potential to drive the reduction of CO₂ to CO. Our finding would provide useful guidance to design and fabricate the stable COF-based Z-scheme heterostructure with well-defined geometry configuration, intimate contact interface and good electron delivery channel for photocatalysis research.

CRedit authorship contribution statement

Y. Wang: Conceptualization, methodology, investigation, formal analysis, writing-original draft, and writing-review & editing. **Z. Hu:** Data curation and formal analysis. **W. Wang and Y. Li:** Data curation and software. **H. He:** Methodology and formal analysis. **L. Deng:** Supervision, conceptualization, methodology, writing-original draft, and writing-review & editing. **Y. Zhang, J. Huang, N. Zhao and G. Yu:** Methodology and formal analysis. **Y. -N. Liu:** Supervision, conceptualization, funding acquisition, writing-original draft, and writing-review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.122419](https://doi.org/10.1016/j.apcatb.2023.122419).

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